SUB A1

TEXTURED SUBSTRATE CAPABLE OF CONSTITUTING A GLAZING, PROCESS FOR THE OBTAINING THEREOF

This invention relates to a textured substrate, that is, one displaying a distinctive relief enabling it to achieve advantageous properties, in particular in the case of a transparent substrate and/or a substrate for which a certain optical quality is sought. These properties reside, among others, in the changing of the behavior of the substrate in wettability into a behavior which may be described as super-hydrophobic/oleophobic or super-hydrophilic/oleophilic, in anti-staining or anti-reflecting properties.

The property of hydrophoby/oleophoby of a substrate consists in that the angles of contact between a liquid and this substrate are large, for example on the order of 120° for water. The liquid then has a tendency to flow easily on the substrate in the form of drops, through simple gravity if the substrate is inclined or under the effect of aerodynamic forces in the case of a vehicle in motion. This phenomenon is the expression of an anti-rain effect. Moreover, the drops are capable of conveying along in their flow dust, insects or more or less greasy dirt of any nature, the presence of which might result in an unsightly appearance or even, as the case may be, an impairment of visibility through the substrate when the latter is transparent. To this extent, the hydrophobic/oleophobic substrate also has an anti-staining property.

Known hydrophobic/oleophobic agents are, for example, fluorous alkylsilanes such as described in patent application EP-A1-0 675 087. They are applied in solution in known manner in accordance with conventional methods of deposition with or without heating.

On the contrary, the hydrophilic/oleophilic property of a substrate is manifested by small angles of contact between a liquid and this substrate, on the order of 5° for water on clean glass. This property promotes the formation of thin transparent liquid films, to the detriment of formation of condensation, or of frost made up of minuscule droplets degrading visibility through a transparent substrate. These anti-condensation effects and anti-frost effects seen on a hydrophilic/oleophilic substrate are well known.

Numerous hydrophilic, in particular hydroxylated, agents such as poly(hydroxyalkyl(meth)acrylates) are used for this purpose, in known manner, for transparent substrates). Certain compounds, known as photocatalytic, such as TiO_2, likewise are used, in particular in combination with glass substrates, not only for their hydrophilic nature following exposure to light, but also for their ability to break down dirt of organic origin by means of a process of radical oxidation; the hydrophilic/oleophilic and anti-staining properties then are achieved simultaneously. It is known to deposit coatings with a photocatalytic property comprising TiO_2 from at least one titanium precursor, if need be in solution, through liquid-phase pyrolysis, through a sol-gel technique or even through vapor-phase pyrolysis.

In accordance with the foregoing, the hydrophobic/oleophobic property is assessed quantitatively by measurement of the angle of contact formed more often than not by a drop of water on a given substrate. If there is no further indication, this angle of contact is measured for a horizontal substrate. In reality, as already noted above, it is the behavior of drops of liquid in dynamics which is addressed by the act of imparting a hydrophoby to a substrate. This also holds

true for approximately vertical static substrates such as the exterior glazing for the building trade, glazing for showers as well as for transportation vehicles. Now, in the case of a drop of liquid on a substrate inclined in relation to the horizontal, two different angles of contact are seen: the angle of advance and the angle of retreat, determined at the front and at the rear of the drop, respectively, in relation to the direction of its travel. These angles are values attained at the limit of disengagement of the drop. The difference between the angle of advance and the angle of retreat is called hysteresis. A drop of water having a high hysteresis or a small angle of retreat likely would have difficulty in flowing on a substrate. Thus it is easily understood that an effective hydrophoby is conditioned by both a large angle of advance and a low hysteresis.

As a matter of fact, on this level the inventors obtained excellent results, never before achieved. On a hydrophobic substrate in accordance with the invention, an exceptionally smooth and rapid flow of water drops was obtained. Moreover, it has been able to be confirmed that the measures set forth in accordance with the invention also are of such nature as to intensify the hydrophilic aspect of a substrate. One of the consequences thereof is, in certain cases, according to the preceding explanations, that the anti-staining aspect attains a very high level.

These results are achieved, in accordance with the invention, by means of a substrate comprising a relief which defines a low surface level and a high surface level, separated by a certain height not less than 1/10 of the characteristic dimensions of the motif forming said high level, the latter representing 1 to 65% of the surface of the substrate.

In fact, such a substrate has proven to be capable of providing super-hydrophobic/oleophobic or super-hydrophilic/oleophilic properties, and in particular with respect to drops of water flowing thereon, a very large angle of advance for a very low hysteresis.

In the variant of the invention in which the substrate is hydrophobic/oleophobic, it preferably comprises an agent selected from among the group consisting of:

a) the silicones, and

b) the compounds corresponding to the formulas:

$$F_3C(CF_2)_m(CH_2)_nSiX_{3-p} \quad (I)$$

and

$$R_pSiX_{4-p'} \quad (II)$$

in which:

- m = 0 to 15;
- n = 1 to 5;
- p = 0, 1 or 2;
- R is a linear or branched alkyl group or a hydrogen atom;
- X is a hydrolyzable group such as a halogeno, alkoxy, acetoxy, acyloxy, amino, NCO group;
- p' = 0, 1, 2 or 3.

According to the second principal variant of the invention, the substrate is hydrophilic/oleophilic because it contains a suitable agent. As a hydrophilic/oleophilic agent there may be cited, as a final product or a precursor, poly(meth)acrylic acid as is or at least partially salified with sodium, potassium, cesium..., nonionic surfactants, esters of cellulose such as hydroxypropyl cellulose, derivatives of chitosan and chitine, polymethacrylates, poly(vinyl alcohols) and poly(vinyl acetate), polypyrrole, polyaniline, poly(acrylamide), poly(N,N-dimethylacrylamide), poly(N-isopropylacrylamide), poly(ethylene glycol), poly(propylene glycol), poly(oxyethylene) with hydroxy or methoxy end functions, poly(allylamine) chlorhydrate, polysaccharide, (branched)dextrans, (linear polysaccharide)pullulan, poly(styrene carboxylic acid) and salt thereof, poly(styrene sulfonic acid), sodium poly(styrene sulfonate), poly(vinyl butyral), poly(2-vinyl-N-methyl pyridinium iodide), poly(4-vinyl-N-methyl pyridinium iodide), poly(2-vinyl pyridine), poly(2-vinyl pyridinium bromide), poly(vinyl pyrrolidone), copolymers obtained

from monomers starting from various polymers indicated above, and in particular sequenced copolymers, certain titanium compounds such as titanium tetraisopropyl or titanium tetraisobutyl, possibly stabilized, for example with acetylacetonate, titanium tetrachloride...

The height of said high surface level in relation to said low surface level preferably ranges between 0.01 and 10 micrometers.

The geometry of the relief with which the substrate is provided may or may not display a periodicity.

In several examples of embodiment of the invention which obtained high performances, said low surface level and high surface level are connected to one another by means of partitions approximately perpendicular to the plane of the substrate.

In accordance with the invention, the relief of the substrate may assume various forms.

According to a first type of form, said high surface level displays a continuity in at least one direction of the plane of the substrate; in this type of form it is implied that the continuity of the high level exists, if not over the entirety of the expanse of the substrate, at least over a substantial proportion of the latter, in relation to said direction in question.

These forms are represented in particular by a relief comprising a multiplicity of approximately identical parallelepipedal objects, parallel and uniformly spaced. In this case there is continuity of the high surface level in a single direction.

A case in which this continuity exists in two directions of the plane of the substrate might be represented by a relief comprising a multiplicity of approximately identical cylindrical craters uniformly distributed on the substrate, their axes being approximately perpendicular to the plane of the substrate (provided that these craters are disposed over a substantial proportion of the expanse of the substrate, as previously specified).

According to a second type of form of the relief, said high surface levels displays no continuity in any direction of the plane of the substrate.

This type is represented in particular by a relief made up essentially of a discrete series of identical or different objects, in particular cylinders with axes approximately perpendicular to the plane of the substrate, notably identical cylinders of revolution uniformly distributed on the substrate.

In accordance with various embodiments of the invention, reliefs have been formed based on at least one compound of at least one of the elements: Si, W, Sb, Ti, Zr, Ta, V, Pb, Mg, Al, Mn, Co, Ni, Sn, Zn, In and/or a plastic possibly containing a filler which may be hardened by means of application of an energy source, or a thermoplastic, at least one underlying portion of the substrate being composed of a glass and/or a plastic (in particular of the type occurring in the customary composition of a glazing, which will be explained in further detail below).

According to a particularly advantageous variant of the invention, the substrate is a conductor of electricity. It then is composed, for example, of sub-stoichiometric and/or doped metal oxides such as described in the application FR 2 695 117.

Examples thereof mentioned in this application are indium oxide doped with tin (ITO), zinc oxide doped with indium (ZnO:In), with fluorine (ZnO:F), with aluminum (ZnO:Al) or with tin (ZnO:Sn) and tin oxide doped with fluorine (SnO_2:F). In addition to their electricity-conducting properties, these materials are described as displaying reflecting properties in the infrared, particularly low-emissivity, range (the case of a transparent substrate). Nonetheless, in the context of this application, the ability of the substrate to conduct electricity applies principally to the antistatic function, that is, the capacity to dissipate electrostatic charges and to prevent the accumulation thereof locally and, to a lesser extent, the formation of heating films, in particular

for de-icing and de-misting of windows. Other electricity-conducting materials which may be used are antimony-doped tin oxide (pentavalent or tetravalent) SnO_2:Sb, a material comprising for example SiH_4 or CH_4 as a precursor in order to form metallic bonds of the Si-Si or C-C type or metallic salts such as copper acetylacetonate. The advantage of preventing local accumulations of electrostatic charges appears in applications such as an aircraft windshield, in which on the contrary it is important to remove these charges by conduction. Accumulations of charges indeed would constitute a source of cracking and destruction of possible stacked functional layers as well as of the very structure of the substrate, in particular when it is laminated or stratified.

The substrate of the invention advantageously displays anti-reflecting properties. This may be obtained by the fact that the characteristic dimensions of the relief on the substrate do not exceed the wavelengths of the visible field, preferably 200 nm, or even 100 nm. Alternatively or additionally, the anti-reflecting properties may derive from a treatment in the form of a stacking of thin interferential layers, generally consisting in an alternation of layers with a base of dielectric material with high and low indexes of refraction. Disposed on a transparent substrate, such a coating has the function of reducing the light reflection thereof, thus of increasing the light transmission thereof.

On the exterior surface of an automobile windshield, for which levels of light transmission, generally in excess of 75%, and a very low residual haziness (less than 1% of the transmitted light) are dictated, the anti-reflecting effect results in the improvement of the visual comfort of the driver and the passengers.

The substrate of the invention preferably displays anti-staining properties. These may derive in part, as has been seen above, from the (super-)hydrophobic/oleophobic or (super-)hydrophilic/oleophilic properties. These properties also may be directly linked to the nature of certain components of the substrate. Thus, among the hydrophilic/oleophilic agents

cited previously, certain titanium compounds, for example TiO_2, are capable of breaking down organic residues through photocatalytic means.

Other subjects of the invention lie in a series of processes for formation of the substrate described above.

A first process is composed of the stages consisting in:

- applying to a support surface a precursor of liquid to viscous consistency, in
- carrying out the molding of a sol-gel from this precursor, then in
- consolidating this through evaporation of solvent, possibly with the aid of an energy source.

A second process is composed of the stages consisting in:

- applying to a support surface a polymerizable and/or cross-linkable plastic composition possibly containing fillers, in particular mineral fillers for reinforcement, in
- performing polymerization and/or cross-linking as well as separation of possible residual components such as solvent, possibly with the aid of an energy source.

Suitable as plastics are numerous thermoplastics of the polyolefin, polyamide, polyvinylbutyral, polyurethane, polymethacrylate, sequenced copolymer... type, as well as conventional thermohardenable or photo-cross-linkable resins with an unsaturated polyester, phenolic, polyurethane... base.

The third main process of the invention is composed of the stages consisting in:

- forming a mask on a surface according to a technique such as serigraphy, ink-jet printing, lithography, in particular photolithography, engraving, for example ionic reactive, or similar,
- attacking, in particular by chemical means, the portions of said surface not protested by this mask, then possibly in
- removing the mask.

According to a fourth process, a film in itself forming said relief is caused to adhere to a support surface. This film may be plastic-, in particular thermoplastic-based.

Each of these four processes terminates:

- either in the formation of a mold which may be used to form the substrate of the invention,

- or in the formation of the substrate itself.

Considering the search for super-hydrophoby/oleophoby or for super-hydrophily/oleophily which gave rise to the invention, it should be specified that the hydrophobic/oleophobic or hydrophilic/oleophilic agents as a rule are applied separately according to two main well-known methods: they may be incorporated into the substrete, that is, integrated into the material of the substrate, or else deposited in the form of a coating on the relief of the substrate. According to this second method, it is known to make up hydrophobic coatings in layers or films of varying thicknesses, in particular so-called monomolecular films the thickness of which corresponds to the length of the molecules which constitute it and attains values as low as a few nanometers up to several tens of nanometers.

As the properties of hydrophoby and hydrophily act against one another, the substrate of the invention generally comprises only one or more hydrophobic/oleophobic agents and one or more hydrophilic/oleophilic agents. Nonetheless, the inventors were able to make the two types of agents coexist in one particularly advantageous embodiment in which a relief of objects made of hydrophobic material, for example with a base of perfluoroalkyl alkyltrialkoxysilane, is formed on an anti-staining Ti_2 support surface. The high surface level then is provided with a hydrophobic aspect contributing subsidiarily to the removal of dirt. In terms of the geometry of the relief, it is not ruled out that a liquid flowing on the substrate may come into contact in part with the low surface level of the relief, characterized by its dual hydrophilic and photocatalytic property. It therefore is possible, by means of an appropriate selection of relief geometry, to take advantage of the synergy of the various components of the substrate so as to promote the removal of liquids from the surface thereof and to ensure a high level of cleanliness in the absence of cleaning.

Transparent substrates are particularly addressed by the invention, another subject of which therefore consists in a glazing made up, at least in part, of the substrate described hereinabove. With the exception of the specificities of the relief according to the invention, it should be understood that the structure of such a glazing is customary, that is in particular monolithic or laminated. This structure involves sheets of glass, layers of plastic: polyvinylbutyral, polyurethane, polycarbonate, poly(meth)acrylate, vinyl acetate/ethylene copolymer... as well as functional or decorative serigraphed films, heating-wire or antenna networks...

The applications for the glazing of the invention are varied: glazing for the building trade (windows), street furnishings (billboards, bus shelters...), for air, marine or land (railroad, road) transportation vehicles, for a screen, a lamp or an electronic display, for interior design, furnishings or household electrical appliances: decorative panels, bathroom furnishings (shower partition), shelf, refrigerator or oven door, display case, vitreous ceramic plate...

Other characteristics and advantages of the invention will become apparent in the description of the example which follows.

EXAMPLE

A small 3-cm x 3-cm silicon plate perfectly flat for a thickness of 0.2 cm is made hydrophobic by grafting of a single layer of fluorosilane $F_3C(CF_2)_9(CH_2)_2SiCl_3$. The angles of contact of water (angle of advance A_a and angle of retreat A_r) are measured by means of a goniometer with a precision in the region of one degree and recorded in the table hereinbelow. To accomplish this, a drop of water is formed on the surface of the small plate by means of a pipette and the angle of advance is measured during the expansion of the drop; in the second phase, the volume of the drop is reduced by gradually drawing up in the pipette the water which forms it, the angle of contact measured during this operation being the angle of retreat.

Then the reliefs represented on the attached Figures 1, 2 and 3 are formed on small plates identical to the aforementioned one, by molding of a tetramethoxysilane sol-gel. After gelling, the silica structure is consolidated at 1100° C for 2 hours and made hydrophobic as indicated above. The molding of the sol-gel is performed in accordance with the instructions in the publication MARZOLIN C. et al. *Advanced Materials* 10 (1998) 571, incorporated into this application by way of reference. The reliefs are designated respectively by the terms "spikes," "craters" and "grooves." According to the invention, these three reliefs define a low surface level and a high surface level separated by a height of not less than 1/10 of the characteristic dimensions of the motifs forming said high level, that is, the diameter of the cylindrical spikes, the distance between two craters and the width of the grooves, respectively. Moreover, for these three forms of relief considered again in the same order, said high surface level represents 5%, 64% and 25% of the surface of the substrate. The characteristic dimensions of the three reliefs are in the region of a micrometer.

The angles of advance and retreat are measured on each of the small plates and recorded in the table hereinbelow.

TABLE

Small plate	A_a (degrees)	A_r (degrees)
Flat	118	100
Spikes	170	155
Craters	138	75
Grooves (perpendicular)	165	132
Grooves (parallel)	143	125

The indications "perpendicular" and "parallel" refer to the directions in which the

measurements of angle of advance and retreat are made with respect to the direction of the grooves.

In comparison with the control constituted by the small flat plate, it is noted that the small plates with reliefs according to the invention in all cases attain a substantial increase in the angle of advance while retaining a hysteresis which is unchanged or changed only slightly. By way of exception, an unfavorable decrease in the angle of retreat is seen in the case of the small plate with craters; this phenomenon probably is linked to the particular geometry of this surface, and might be interpreted as the expression of a "suction" effect exerted by the craters, which might hold back the water in its flow. The fact remains that the other values obtained express an exceptionally high degree of the hydrophobic nature, clearly superior to that of the small flat plate.